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COVER SHEET FOR FILING PROVISIONAL PATENT APPLICATION (37 CFR 1.51(c)(1))

Box Provisional Application
Assistant Commissioner for Patents
Washington, DC 20231

Date: March 4, 1999

This is a request for filing a PROVISIONAL PATENT APPLICATION under 37 C.F.R. § 1.53(c).

Docket No.	9052-18PR2
Type a plus sign (+) inside this box →	+

INVENTOR(s)/APPLICANT(s)

Timothy N. Milner, Rebecca A. Robbins, Robert G.G. Holmes of BNFL, Derwentwater Pavilion, Westlakes Science and Technology Park, Moor Row, Cumbria, CA24 3JX, UK

Stuart Shealy, Edward Morren of IT Corporation, Knoxville, Tennessee

Colin R. Austin of MSC, Oak Ridge, Tennessee

TITLE OF THE INVENTION *(280 characters maximum)*

TREATMENT OF RADIOACTIVELY CONTAMINATED METALS

ENCLOSED APPLICATION PARTS *(check all that apply)*

- ☒ Specification (Number of Pages 10)
- ☒ Drawing (Number of Sheets 3)
- ☒ Claims (Number of Claims 1)
 (A complete provisional application does not require claims 37 C.F.R. § 1.51(c)).
- ☐ Small Entity Statement
- ☐ Other:

CORRESPONDENCE ADDRESS

Kenneth D. Sibley
Registration No. 31,665
Myers Bigel Sibley & Sajovec
PO Box 37428
Raleigh NC 27627
Tel. (919) 854-1400
Fax (919) 854-1401

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Respectfully submitted,

Kenneth D. Sibley
Registration No. 31,665

Correspondence Address:
USPTO Customer Number: **20792**
Myers Bigel Sibley & Sajovec
PO Box 37428
Raleigh NC 27627
Tel. (919) 854-1400
Fax (919) 854-1401

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TREATMENT OF RADIOACTIVELY CONTAMINATED METALS

FIELD OF THE INVENTION

This invention relates to the treatment of radioactively contaminated metals. For instance the present invention may be applied to the treatment of metal components which have been used in the nuclear power industry and have become radioactively contaminated. Such components can be cleaned using a combination of physical and chemical techniques following which they may be released onto the scrap metal market or melted and formed into plate or billets for recycling.

BACKGROUND OF THE INVENTION

A chemical decontamination process utilises a series of immersion tanks to remove fixed radionuclides from the surface of metal components. Acid solutions contained in these immersion tanks dissolve scale, corrosion products and some base metal to effect removal of surface contamination. The various metal species and radionuclides accumulate in the immersion tanks and, as a result, performance deteriorates and the decontaminant must be changed.

STATEMENT OF INVENTION

The present invention provides a flexible, robust decontamination and waste treatment process enabling high throughput in a minimal cost operating regime. The process of the invention is capable of generating a significant volume of radioactive scrap metal (RSM), ranging from PWR Inconel components, which are contaminated with activation and fission products, to aluminium components contaminated with transuranics.

According to the present invention there is provided a method of treating a radioactively contaminated metal object comprising contacting the object with an acid solution to cause dissolution of a surface layer of the metal object, and treating the resultant solution to cause the dissolved metal to separate from the solution in solid form.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 of the accompanying drawings is a flow diagram of a decontamination process in accordance with the present invention. As indicated in Figure 1, the process involves various unit operations. The incoming radioactive scrap (RS) is subjected to segregation and size reduction. It is then sentenced for physical chemical decontamination. Processing takes place through the decontamination line and a radionuclide contamination survey of the processed metals is carried out. The decontaminated metals are sent for recycling, disposal as LLW or sale into the scrap market. The spent decontamination liquor is treated and this results in solid/liquid separation. The process liquors are treated to meet the local sewer discharge limits. Process sludges are immobilised for disposal as non-RCRA dry active waste.

It is of importance in the context of the present invention that the chemical decontamination stage or stages provide a safe and cost effective process for the decontamination of RSM. The chemical decontamination should be capable of accepting a wide variation in feedstock and offer a cost saving over direct disposal of RSM. There should be produced a minimal volume of non RCRA secondary waste and the process liquors should be suitable for discharge to the local sewer.

Preferably the acid solution providing the decontamination of liquor comprises nitric and hydrofluoric acids which enable decontamination to be carried out on a varied or variable feedstock at high throughput levels. The aggressive nature of the nitric/hydrofluoric acid decontamination process requires careful control of the process parameters to achieve an optimum surface corrosion rate for a given substrate. Such optimising has various advantages. Base metal corrosion is kept to a minimum. The lifetime of the decontamination tank or tanks is prolonged. Uniform surface corrosion takes place without pitting of the base metal. The volumes of secondary waste are minimised by avoiding dissolution of uncontaminated base metal. There is also an avoidance of uncontrolled dissolution reactions which gives rise to off gases as the acids break down.

In order to achieve the optimal surface corrosion rate for a varied feedstock using a single chemical decontaminate, there is required a careful control of the temperature of the decontamination tank, the concentrations of the mixed acid treatments solution, the agitation and the oxidation potential of the decontaminant, the concentration of the dissolved metals and radionuclides in the decontamination tanks and the sequencing and immersion time in the decontamination tanks.

As fresh acid solution contacts a contaminated metal surface, dissolution occurs and the metal is dissolved in the acid solution. This results in metal loading of the acid bath. Although the reaction of the acids upon the metal surface is complex and involves a number of equilibrium reactions, the dissolution of iron by nitric acid can be simplified to the following reaction:-

$$Fe^{2+} + 2HNO_3 = Fe(NO_3)_2 + 2H^+ \text{ and } Fe^{2+} + 2HF = FeF_2 + 2H^+$$

Similar reactions take place with other metals such as:-

$$Cr^{3+} + 3HNO_3 = Cr(NO_3)_3 + 3H^+$$
$$Fe^{3+} + 3HNO_3 = Fe(NO_3) + 3H^+$$
$$Al^{3+} + 3HF = AlF_3 + 3H^+$$
$$Ni^{2+} + 2HF = NiF_2 + 2H^+$$

In the case of the dissolution of iron by nitric acid, there is a theoretical requirement for two moles of nitric acid to dissolve one mole of iron. However due to passivation of the metal surface, plate-out, oxidation of iron and the extremely slow dissolution rate as the acid is consumed in the dissolution reactions, such metal loading is impractical.

As a first order approximation, the metal dissolution rate of the acids is directly proportional to the concentration of the acids. Accordingly, for a high throughput of

metal in the decontamination line, two factors have a significant impact on decontamination performance. First, the overburdening of the acids with dissolved metals results in insufficient unreacted acid to achieve significant dissolution of the metal substrate. Secondly unreacted acid in the spent liquor has to be neutralised during waste treatment and this generates a significant volume of secondary waste.

Accordingly, the operation of the decontamination process of the present invention has involved a balance which has been struck between metal loading of the acids and dissolution rates, taking into account the potential for surface pitting and off gas production. It is important to minimise the production of off gasses that require scrubbing, thereby resulting in the generation of a secondary waste form and depletion of the acid capacity. This is particularly important when decontaminating the more reactive metals such as carbon steel and aluminium.

In order to obtain the optimisation mentioned above, it is preferred that the process is operated using a plurality of decontamination tanks in a manner referred to as "lag" basis. This procedure involves designating the decontamination tanks as low, medium and high dissolved metal content, each fulfilling a particular duty within the overall decontamination process. The low tank is used for final polishing of the decontaminated metal as this tank has the lowest radionuclide inventory and the highest dissolution kinetics. The high tank is used for initial decontamination where the highest levels of radionuclides, associated with the outermost surface, are removed. The medium tank is a transitional tank which is additionally used for "special" materials, which are substantially different from other materials of the feedstock. The use of the medium tank is optional.

During the process, the tanks are rotated from low to high based on a predetermined dissolved metal and radionuclide inventory. The high tank is taken off line and designated as spent once decontamination has become ineffective. In order to establish this there is carried out a regular sampling and analysis procedure to measure and record trends in tank performance. The procedure may be simplified

with the cost of analysis reduced by using the experience gained from operating the process to devise a "finger print" which can be used to determine when a tank should be reclassified.

The operational flexibility of the chemical decontamination line allows both decontamination for recategorisation to LLW and also to free release. The economic case for free release or recategorisation has to be considered. In the case of a PWR primarily loop component which has been exposed to a high temperature, high pressure liquid environments generally require the removal of 20 to 30μm of corrosion film and base metal to achieve recategorisation to LLW. Achieving free release levels can require the removal of an additional 150 to 200μm of metal. Components from fuel cooling pools such as stainless fuel racks can be decontaminated to LLW by removing 5 to 8μm surface and free release can be achieved by removing 15μm of surface metal. The less demanding metal removal could favour free release.

The tank lag system allows decontamination to free release to be performed in the low activity tank and decontamination for recategorisation to LLW to be performed initially in the high and subsequently in the medium activity tank.

An additional advantage of the lag system is the degree of uniformity, in terms of dissolved metal and radionuclide content, that is introduced to the spent tank waste treatment process.

The spent acid resulting from the decontamination stage or stages may be subjected to a number of treatment steps. Treatment of the spent acids produces two waste streams. One is an alkaline wastewater which, after final polishing by chelant oxidation followed by ion exchange, is discharged to the local sewer. The other is a sludge containing the major metal species (iron, chromium, nickel) and radionuclides (cobalt, cesium) which may be directly solidified by grouting with, for instance, Portland cement to meet the appropriate waste acceptance criteria.

The spent acids from the chemical decontamination process contain a high concentration of dissolved metals and radionuclides, as illustrated in the following table:

Contaminant	Cr	Ni	Fe	Cu	^{60}Co	$^{134/137}Cs$	^{241}Am ^{54}Mn	Anions (nitrate fluoride chloride)
Concentration	1600 mg/L	2000 mg/L	12,500 mg/L	2000 mg/L	80,000 pCi/L	3000 pCi/L	1000 pCi/L	>10%

In treating the spent acids solution, the aim is to produce a minimal volume of non-RCRA solid waste. Since the composition of the metal component which is treated in the chemical decontamination stage affects the ratios of metals in the spent acid, a highly flexible approach is required. The waste treatment process may be either a batch process or a continuous process although reference will be made hereinafter to a batch process.

The waste treatment process may involve various steps as illustrated in Figure 2 of the accompanying drawings. As illustrated the spent acids solution is partially neutralised and conditioned using calcium hydroxide. The pH is then adjusted to a value in the range of from 9 to 10 using sodium hydroxide. Flocculation is then effected by seeding with inorganic adsorbents causing resultant coprecipitation of metals and radionuclides. Polymers are then added to aid gravity settling of solids. The solids and liquid are then separated and the solids are subjected to grouting. The wastewater liquid is then treated by means of UV/sodium hypochlorite to cause oxidation of chelate. Finally the waste water is polished by ion exchange using clinoptillolite as the resultant liquid is discharged to a local sewer.

The above described process steps may be performed sequentially over a 24 hour period and the acid tank, when empty, is replenished with fresh acid and returned to service. The above described treatment process is both robust and simple to operate and uses readily available, low cost chemicals and process equipment.

Calcium hydroxide is used principally to condition the metal hydroxide floc by assisting in the binding of leachable metals, principally chromium. The calcium fluoride formed in the partial neutralisation forms the body of the floc and improves sludge settling characteristics. The calcium hydroxide is not used for pH control as this may result in the formation of an excessive amount of calcium sludge requiring disposal as a secondary waste product. Accordingly pH adjustment is carried out using sodium hydroxide, which is highly soluble and results in a sharp inflection point in pH, thereby allowing greater process control.

The presence of dissolved iron assists in chromium removal due to the Fe (II)↔Fe (III) couple ensuring the chromium is present in reduced Cr (III) state. In some cases, when the Fe (II)/Cr ratio in the spent acid is less than 4:1 wt/wt, additional ferrous iron may be required to reduce chromium to the less soluble form. This can also be controlled by management of the processing of nickel/chromium alloys and stainless or carbon steels in order to supply the appropriate iron ratio needed for chromium reduction.

The above described two-stage neutralisation results in the formation of a floc which contains virtually all the radionuclide and metal contaminants with the exception of cesium which is highly soluble. Typically cesium is removed from the wastewater by means of an ion exchange column. However such an approach has a number of disadvantages. The processing is slow due to the slow kinetics of the reactions. The highly selective ion exchange media which is required for column use in high salt streams is expensive. Less selective ion exchange media were rapidly exhausted by other metals and radionuclides, producing excessive secondary waste. Pretreatment to remove particulate which has the potential to bind the columns is required and this produces an additional waste stream.

In a preferred method according to the present invention cesium removal is affected using nickel hexacyanoferrate (HCF). A solid HCF ion exchanger is added in the

amount of 300 ppm as a dilute slurry directly into the batch treatment tank once the pH has been adjusted. Cesium removal is aided by isotopic dilution by adding 10 ppm of non-radioactive cesium chloride. Preferably the HCF is used immediately after it has been formulated. Lower cesium removal and higher residual nickel resulted if the HCF is aged.

The kinetics of the cesium complexation with HCF is very rapid and the complex formed is removed from solution by adsorption and agglomeration with the metal hydroxide floc. A decontamination factor of 600 has been achieved for cesium and the supernant liquor was free of all metals except a few ppm of nickel and chromium and trace levels of cesium. Final cesium removal was accomplished by adsorption on clinoptillolite, a natural zeolite.

Separation of the floc from the supernatant can be achieved by the use of mechanical separation devices. However such devices are either costly, generate a secondary waste in the form of a filter media or require frequent manual intervention. Accordingly it is preferred to make use of gravity settling and decanting. In order to speed the stages of the process, several hundred ppm of an anionic polymer was added to increase the rate of settling and the clarity of the supernatant. More preferably, the tank content are rotated using a stirrer device.

After a period of 4 to 8 hours the supernatant from the HCF step was decanted and processed through the waste water treatment polishing step. The solution was dosed with 0.25 to 0.5% sodium hypochlorite and treated with UV light to oxidise the soluble heavy metal complexes (nickel and cobalt-60). Insoluble compounds are produced. The treatment time was from 6 to 18 hours. The particulate is removed by mechanical filtration by passing the material through a bed of sand and charcoal followed by cartridge filters.

As a result the concentration of heavy metals, primarily nickel, is reduced from 10 to 20 mgL to the required discharge limit of not greater than 1.5 mg/L. The ^{60}Co was

similarly reduced from 20 to 50 pCi/L to the required discharge limit of less than 1 pCi/L.

If necessary, further cesium removal may be achieved by mixing the decant liquor with laundry water from the final effluent tank. This dilution lowered the concentration of nitrate and fluoride salts in the wastewater and improved the efficiency of the cesium removal by ion exchange using two columns packed with clinoptillolite. The clinoptillolite column had a residence time of 60 to 80 minutes and the resulting wastewater met local discharge criteria. The capacity of the ion exchange column was found to be between 80,000 to 90,000 bed volumes and the sand bed filter did not require to be changed out.

The second waste stream from the WTS comprises the radionuclide and metal contaminated sludge from the settling and decanting step. This sludge or metal floc was directly solidified in a cemeticous grout. This was achieved by pumping the settled solids from the batch treatment tank into 55-gallon drums. A helical drum mixer was used to incorporate 0.75 to 1.0 pounds of portland cement per pound of sludge. This was accomplished with 20 to 30 minutes mixing and there was only a small heat rise during this process. The grout was then pumped from the drums into moulds that were designed to produce a final waste form meeting local acceptance criteria for size requirements for debris. The resulting grouted waste was produced with a minimal volume increase of 20%. It was cured overnight with no bleed and had a strength of over 50 psi.

P15734

Claims

1. A method of treating a radioactively contaminated metal object comprising contacting the object with an acid solution to cause dissolution of a surface layer of the metal object, and treating the resultant solution to cause the dissolved metal to separate from the solution in solid form.

AMENDED SHEET

Fig. 1 Flow diagram of Decontamination Process

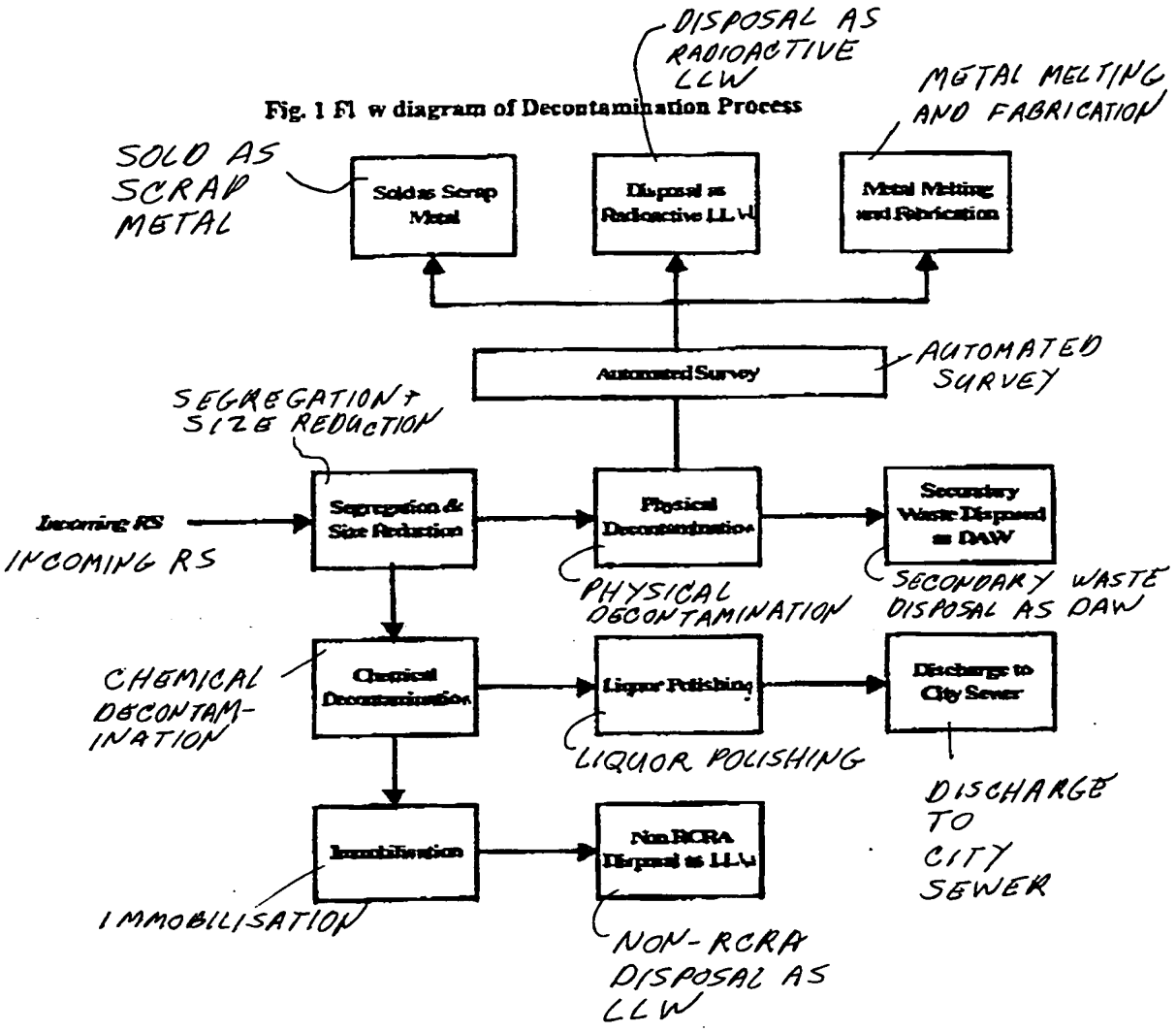
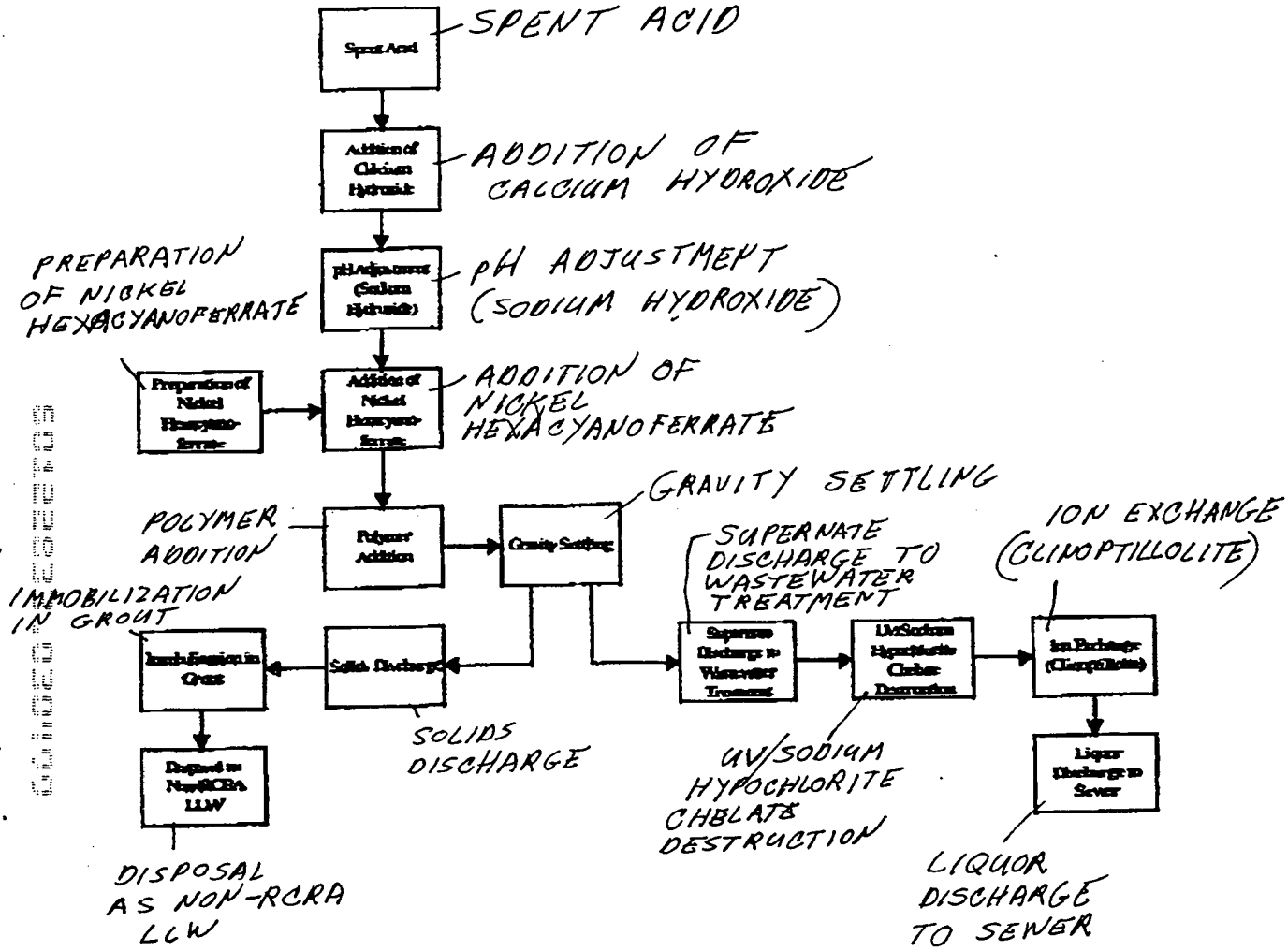


Fig. 2 Flow diagram of Waste Treatment Process



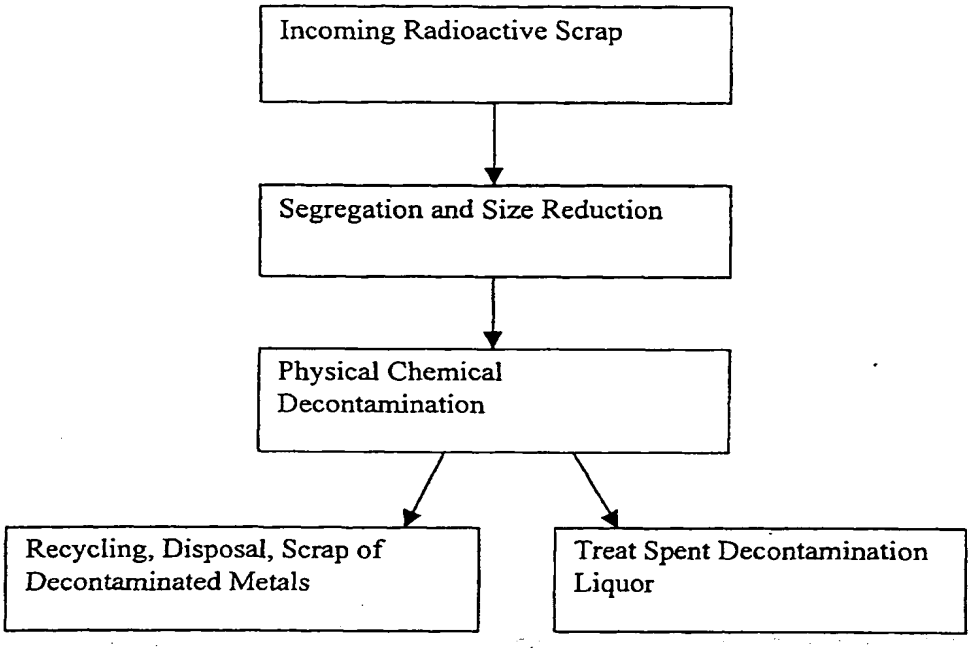


Figure 1

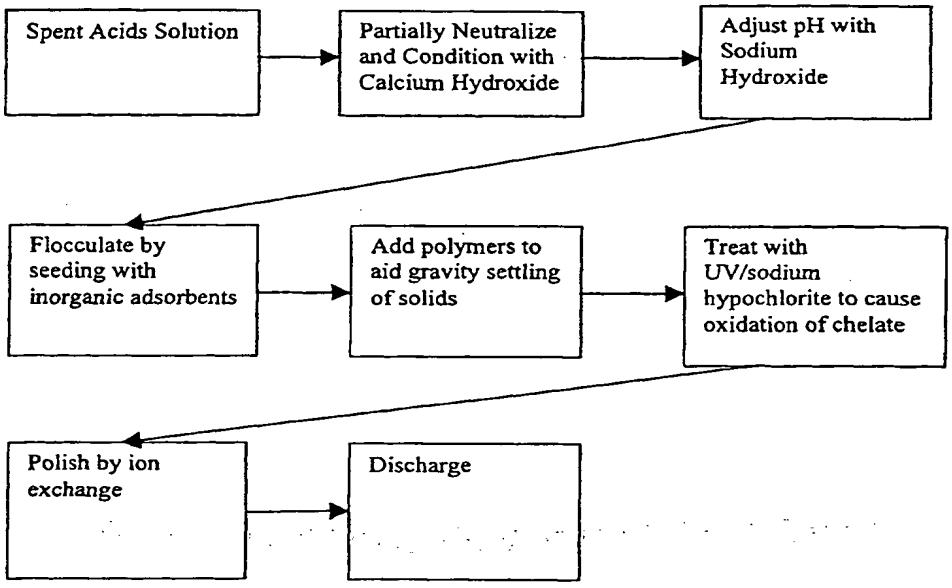


Figure 2